

REE PARTITIONING IN LUNAR MINERALS. J. F. Rapp¹, T. J. Lapen³ and D. S. Draper², ¹Jacobs, NASA Johnson Space Center, Houston, TX 77058 (jennifer.f.rapp@nasa.gov), ²Department of Earth and Atmospheric Sciences, University of Houston, Houston TX 77204, ³NASA Johnson Space Center, Houston, TX 77058

Introduction: Rare earth elements (REE) are an extremely useful tool in modelling lunar magmatic processes. Here we present the first experimentally derived plagioclase/melt partition coefficients in lunar compositions covering the entire suite of REE.

Positive europium anomalies are ubiquitous in the plagioclase-rich rocks of the lunar highlands, and complementary negative Eu anomalies are found in most lunar basalts. These features are taken as evidence of a large-scale differentiation event, with crystallization of a global-scale lunar magma ocean (LMO) resulting in a plagioclase flotation crust and a mafic lunar interior from which mare basalts were subsequently derived. However, the extent of the Eu anomaly in lunar rocks is variable. Fagan and Neal [1] reported highly anorthitic plagioclase grains in lunar impact melt rock 60635, 19 that displayed negative Eu anomalies as well as the more usual positive anomalies. Indeed some grains in the sample are reported to display both positive and negative anomalies. Judging from cathodoluminescence images, these anomalies do not appear to be associated with crystal overgrowths or zones.

Oxygen fugacity (fO_2) is known to affect Eu partitioning into plagioclase, as under low fO_2 conditions Eu can be divalent, and has an ionic radius similar to Ca^{2+} - significant in lunar samples where plagioclase compositions are predominantly anorthitic. However, there are very few experimental studies of (REE) partitioning in plagioclase relevant to lunar magmatism. All but a few studies of plagioclase/melt partitioning focused on terrestrial compositions from basalt to rhyolite, with plagioclase no more anorthitic than An_{85} [2], whereas plagioclase in lunar samples is typically more calcic and melt compositions far more primitive. Only two **measurements** (not studies) of plagioclase D_{Eu} have been reported from experiments using lunar materials [3,4], and because most previous experimental studies concerned terrestrial materials, their fO_2 was generally more oxidized than is typical for the Moon. One potential mechanism to produce the variable Eu anomalies observed in 60635 is by the variation in melt fO_2 by the introduction of oxidized material during impact [1]. Oxidation of the melt would lead to decreased abundance of reduced Eu^{2+} , and therefore decreased incompatibility of Eu in anorthitic plagioclase, producing negative Eu anomalies. The dearth of available data on $D_{Eu}^{plagioclase/melt}$ in lunar compositions

($An > 85$), however, makes this mechanism difficult to assess.

We report results from REE partitioning experiments on plagioclase-saturated Apollo 14 high-alumina basalt 14072. Our results greatly expand the existing plagioclase D_{REE} database for lunar compositions, and investigate the significance of fO_2 in Eu partitioning, and in the interpretation of Eu anomalies in lunar materials.

Experimental: Starting composition was synthesized from mechanical mixtures of anhydrous oxides and carbonates. After decarbonation at 800°C in air, 200ppm REE were added to the mixture using ICP-MS standard solutions and remixed. The mixture was then dried and heated to 1400°C in a Deltech CO-CO₂ gas mixing furnace at the iron-wüstite (IW) buffer. The resultant glass was then re-ground for 30 minutes to ensure homogenization. Experiments were run at 1 bar using CO-CO₂ gas mixtures to buffer the experiments at either IW or fayalite-magnetite-quartz (FMQ) buffer. The experiments were heated to 1400°C, above the liquidus, for 1 hour, and then cooled to the temperature of interest where they were held to equilibrate for at least 72 hours.

Major and minor element data was collected using the JEOL 8530F electron microprobe at NASA Johnson Space Center, and trace element data was subsequently collected using LA-ICP-MS at University of Houston.

Results: Two successful experiments are discussed here: Eu14-12 and Eu14-13. Eu14-12 was buffered at FMQ and equilibrated at 1100°C. Eu14-13 was buffered at IW and equilibrated at 1125°C. Both charges are coarsely crystalline ($>60\mu m$) with melt pools $>100\mu m$ diameter, and therefore are appropriate for analysis by LA-ICP-MS. Both experiments have similar mineralogy, consisting of anorthitic plagioclase (An_{99} at FMQ, An_{89-92} at IW), pigeonite pyroxene (Wo_{11-25} at FMQ, Wo_{12-20} at IW), olivine (Fo_{75} at QFM, Fo_{58} at IW) and glass. Eu14-12 (FMQ) has crystallized to a lesser extent (60% glass) than Eu14-13 (IW) (27% glass).

Chondrite normalized REE abundances in the glass (fig. 1)[6] are similar at both oxygen fugacities. In plagioclase the abundances of the heavy REE (HREE) are more variable than are the light REE (LREE). In run Eu14-13 (IW – black), plagioclase shows two distinct REE patterns, with some grains having an enrichment in HREE. These two distinct groups are also reflected

in the calculated plagioclase/melt partition coefficient (fig. 2). There is currently no clearly observable difference between the grains displaying these different characteristics – further analytical and imaging work is required to determine the crystal-chemical control on this partitioning behavior.

Contrary to the experiments of Aigner-Torres et al [6] in terrestrial basaltic systems, there is virtually no difference in D_{Eu} at different fO_2 conditions using lunar basalt 14072. The plagioclase grains in our experiments are, however, significantly more An-rich (An_{89-99}) than those of [6] (An_{77}). The measured partition coefficients range over half an order of magnitude in the light REE (LREE) and by an order of magnitude in the heavy REE (HREE) (fig. 2), variability similar to that in the available literature data (gray field) [2-4,7-12], although the variability of D_{LREE} in the literature is higher than our experimental data.

We have also measured new REE partition coefficients for pigeonite at IW and QFM, and for olivine at QFM. Olivine/melt D_{REE} are low, ranging from 0.00003 for LREE to 0.01 for HREE. D_{REE} for pigeonite are generally higher than [13] determined for lunar orthopyroxene, although the patterns are very similar (fig.2). D_{REE} is lower at QFM than at IW, and falls between literature data for opx and cpx [14-20], likely due to the intermediate composition of the pigeonites in our experiments.

Implications: Our experiments show that changing fO_2 in a lunar melt is unlikely to produce significantly different Eu anomalies in plagioclase grains crystallizing from that melt. Therefore the variation in Eu anomaly observed by [1] is more likely the result of closed system distillation processes in the impact melt pool, where because of its extreme compatibility in plagioclase Eu is exhausted from the melt in the immediate vicinity of a growing grain, resulting in incorporation of a negative Eu anomaly.

Our results are the first experimentally derived plagioclase/melt partition coefficients in lunar compositions covering the entire suite of REE. We also report D_{REE} for olivine and intermediate pyroxene compositions, greatly increasing the partition coefficient database at lunar conditions, and will enhance efforts at modelling lunar magmatic processes.

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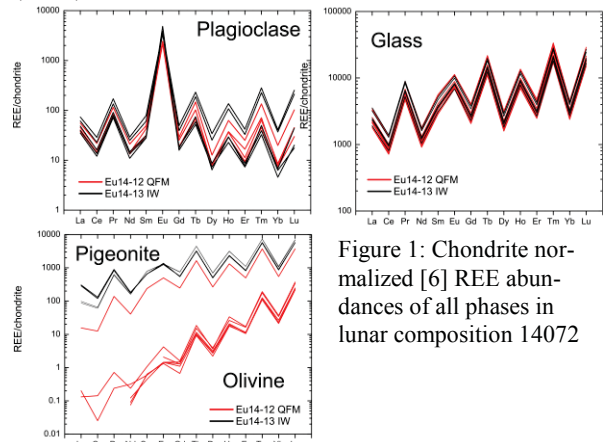


Figure 1: Chondrite normalized [6] REE abundances of all phases in lunar composition 14072

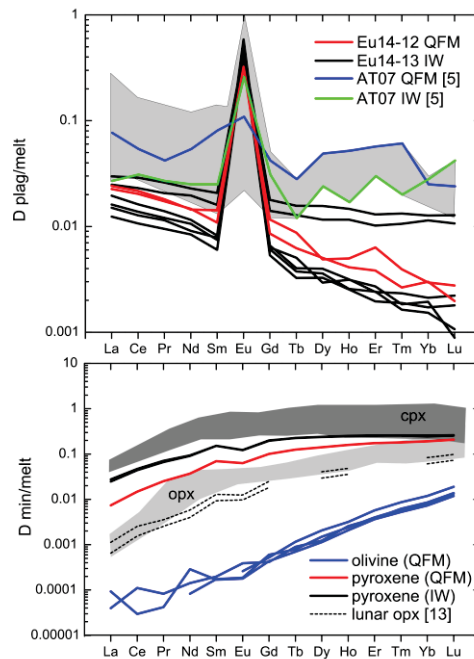


Figure 1: REE partition coefficients for experimentally grown plagioclase (top) and olivine and pigeonite (bottom) in lunar composition 14072 compared to literature data [2-1]